# PATENT SPECIFICATION

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1 208 908

## (54) PENTACOORDINATE SILICON COMPLEXES

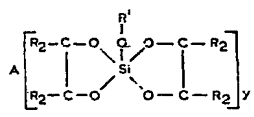
(71) We, DOW CORNING CORPORATION, of Midland, Michigan, United States of America, a corporation organized under the laws of the State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pentacoordinate silicon complexes and methods for their preparation.

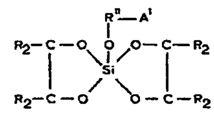
Extracoordinate silicon complexes have been known to exist for quite some time (see United Kingdom Patent Specification No. 1,077,939 and the references cited therein). In the Journal of the American Chemical Society, *86*, 3170 (1964), it was disclosed that hexacoordinate silicon complexes like those prepared by Rosenheim et al. can be prepared by reacting ethyl silicate, catechol and an amine. It was also disclosed, as in the above mentioned patent, that pentacoordinate silicon complexes can be prepared by reacting an appropriate trialkoxysilane with catechol and an amine. It was further taught in footnote (6) of the article in the Journal of the American Chemical Society that pentacoordinate silicon complexes could be prepared by reacting an appropriate trialkoxysilane with an aliphatic 1,2-diol (a vicinal diol) and an amine. It would be expected from these teachings that if one reacted ethyl silicate, an aliphatic 1,2-diol and an amine, one would obtain a hexacoordinate silicon compound. It has been found, however, that when one carries out such a reaction that there is unexpectedly produced a pentacoordinate silicon complex.

The present invention provides pentacoordinate silicon complexes of the general formulae

(1)



and



(2)

in which each R is a hydrogen atom or a monovalent radical attached to the carbon atom via a carbon to carbon bond or two R radicals on adjacent carbon atoms may taken together represent a divalent radical attached to the adjacent carbon atoms via carbon to carbon bonds;

R′ is a monovalent radical attached to the oxygen atom via a carbon to oxygen bond;

A is a cation formed from an amine or ammonia;

y is an integer equal to the valency of the cation A;

R″ is a divalent radical attached to the oxygen atom via a carbon to oxygen bond; and

A′ is a quaternary ammonium group.

R can be, for example, alkyl, alkenyl, cycloalkyl, aryl, aralkyl or alkaryl radicals; the corresponding halogenated radicals; the corresponding amino and cyano substituted radicals; and the corresponding carboxy substituted radicals. In addition two R radicals on adjacent carbon atoms can taken together represent

a divalent hydrocarbon radical. It is preferred that the R radicals be hydrogen atoms or contain from 1 to 18 carbon atoms. Specific examples of R radicals are the methyl, ethyl, propyl, butyl, amyl, hexyl, 2-ethylhexyl, decyl, dodecyl, octadecyl, eicosyl, heptacosyl, vinyl, allyl, hexenyl, cyclohexyl, phenyl, xenyl, naphthyl, benzyl, 2-phenylethyl, tolyl, boromomethyl, trifluoromethyl, chlorocyclohexyl, aminophenyl, cyanophenyl, carboxyphenyl, aminoxenyl and carboxyethyl radicals.

In the first formula the R′ radical is a monovalent radical attached to the oxygen atom via a carbon-to-oxygen bond. Thus the R′ radical can be any of those radicals illustrated for R above. Preferably R′ is an alkyl radical containing from 1 to 6 carbon atoms. Similarly in the second formula R″ is a divalent radical attached to the oxygen atom via a carbon to oxygen bond and is preferably an alkylene radical with from 1 to 6 carbon atoms.

In the first formula A is a cation formed from ammonia or an amine. The amine can be a primary, secondary or tertiary aliphatic or aromatic amine, an alkanol amine, a quaternary ammonium compound, or any other similar amino type compound. Specific examples of amines that can be used include methylamine, ethylamine, propylamine, isopropylamine, butylamine, amylamine, hexylamine, decylamine, dodecylamine, octadecylamine, dimethylamine, diethylamine, methylamylamine, triethylamine, tripropylamine, diethylmethylamine, cyclohexylamine, benzyldimethylamine, aniline, dimethylaniline, toluidine, ethanolamine, diethanolamine, triethylamine, ethylenediamine, cadaverine, hexamethylenediamine, diethylenetriamine, pyridine, guanidine, tetramethyl-guanidine, melamine, tetramethylammonium hydroxide, trimethyl-beta-hydroxyethylammonium hydroxide, benzyltrimethylammonium hydroxide, cetyltrimethylammonium hydroxide, tallow-trimethylammonium hydroxide and 2,4,6-tri-(dimethylaminoethyl) phenol. Ammonia or ammonium hydroxide can also be used.

A particular embodiment of this invention occurs when the cation is present in the molecule bonded directly to the —OR′ substituent as shown in formula 2. This embodiment is specifically illustrated in Examples 2, 3 and 6 below.

During the formation of the complexes of this invention one or more of the nitrogen atoms of the amine becomes protonated thus forming the cation A. For example, a polyamine such as ethylenediamine can form either the monovalent $H_2NCH_2CH_2NH_3^{\oplus}$ cation or the divalent $^{\oplus}H_3NCH_2CH_2NH_3^{\oplus}$ cation. The portion of the complex shown in brackets in the above formulae 1 is a monovalent anion. The number of cations and anions in the complex is such as to provide an overall neutrality. Stated another way, there is an equal number of positive and negative charges in the complex. By way of example, when cation A is monovalent, the anion also being monovalent there must be one of each and when the cation A is divalent there must be two anions in the complex.

The compounds defined by formula 1 above can be prepared by a process which comprises reacting

1) a compound of the formula $(R'O)_4Si$ wherein R′ is as defined above;

2) a vicinal aliphatic diol of the formula

$$\begin{array}{l} R_2C\text{—}OH \\ \quad | \\ R_2C\text{—}OH \end{array}$$

wherein R is as defined above; and

3) ammonia or an amine.

The compounds defined by formula 2 above can be prepared by a similar process which comprises reacting

1) a compound of the formula $(R'''O)_4Si$ wherein R‴ is a monovalent radical attached to the oxygen atom via a carbon to oxygen bond;

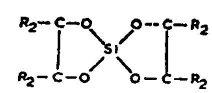
2) a vicinal aliphatic diol of the formula

$$\begin{array}{l} R_2C\text{—}OH \\ \quad | \\ R_2C\text{—}OH \end{array}$$

wherein R is as defined above; and

3) an amino alcohol of the formula OH—R″—A″ wherein R″ is as defined above and A″ is an amino group which on quaternisation gives the quaternary ammonium group A′.

In addition compounds of both formulae (1) and (2) above can be prepared by a process which comprises reacting a silicon compound of the formula



wherein each R is as defined above with either

(1) an alcohol of the formula R′OH wherein R′ is as defined above and ammonia or an amine; or

(2) an amino alcohol of formula OH—R″—A″ wherein R″ is as defined above and A″ is an amino group which on quaternisation gives the quaternary ammonium group A′.

The reactions are generally carried out in a suitable solvent, polar solvents such as acetonitrile being preferred, and the reaction conditions can range from simply combining the reactants at ambient temperature to boiling the mixture.

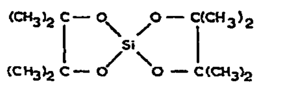
The various compounds used in the process

described above including the silicates and vicinal diols are materials well known in the art.

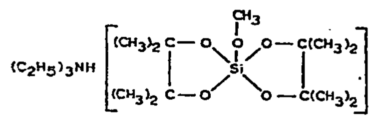
The invention is illustrated by the following examples in which all percentages are on a weight basis unless otherwise specified.

EXAMPLE 1

To 2.60 g. of



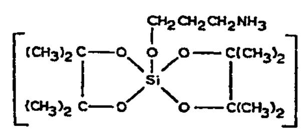
and 2.02 g. of triethylamine there was added 0.64 g. of methanol which caused the crystalline spirosilicate to exothermally dissolve. Upon cooling in a refrigerator, crystallisation occurred. The supernatant liquid was decanted, the crystalline solid quickly washed with pentane, and then evacuated free of residual volatile solvent. The resulting product was



and found to have a neutral equivalent of 416 (theoretical 393).

EXAMPLE 2

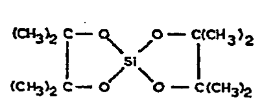
A solution of 20.8 g. of $(C_2H_5O)_4Si$, 23.6 g. of pinacol and 7.5 g. of 3-aminopropanol-1 in 50 g. of acetonitrile was heated at reflux for 50 hours. After cooling to room temperature, the crystalline product was removed by filtration, washed with a little acetonitrile, and then vacuum dried. The product was



and found to have a neutral equivalent of 339 (theoretical 335).

EXAMPLE 3

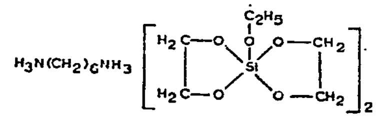
To a solution of 2,60 g. of



in 10 cc. of benzene there was added 0.75 g. of 3-aminopropanol-1 which resulted in the immediate and exothermic deposition of a crystalline solid. This solid was isolated by filtration, washed well with hexane, and vacuum dried to give a quantitative yield of 3.3 g. of the zwitterion product of Example 2. This product had a melting point of 190—195°C. and a neutral equivalent of 336. The infrared spectrum of this product was identical to that of the product of Example 2.

EXAMPLE 4

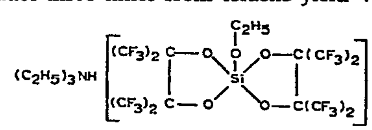
To a 250 ml. suction flask there was added 20.8 g. of $(C_2H_5O)_4Si$, 15.5 g. of ethylene glycol, 5.9 g. of hexamethylenediamine and 35 cc. of acetonitrile. A white crystalline solid formed immediately as the reactants were swirled together. After boiling for one hour, the solid was removed by filtration, washed with fresh acetonitrile, and then vacuum dried to obtain 15 g. of the crystalline product



which was found to have a neutral equivalent of 252 (theoretical 251).

EXAMPLE 5

To one ounce vial there was added 2.1 g. of $(C_2H_5O)_4Si$, 10 g. of perfluoropincaol and 3.03 g. of triethylamine. The addition of the amine was accompanied by the evolution of much heat and upon subsequent cooling to room temperature the vial contents crystallised. This material was filtered, washed with hexane, and then evacuated to constant weight to obtain 11 g. of the simple crystalline triethylamine salt of perfluoropincaol. 10 g. of this salt was then heated for one hour at 140—150°C. with 2.1 g. of $(C_2H_5O)_4Si$. Recrystallisation of the resulting dark coloured product three times from toluene yield 4 g. of



which was found to have a neutral equivalent of 859 (theoretical 839). It is noted that this and the other fluorinated products of this invention are initially neutral in glacial acetic acid, but are titratable as bases upon long standing at room temperature or upon heating at reflux.

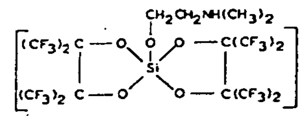
This complex was found to be very soluble in oxygenated solvents such as tetrahydrofuran, acetic acid, alcohols and acetone, and only poorly soluble in aliphatic hydrocarbons.

Elemental analysis of the product gave the following results:

| | %C | %H | %F | %Si |
|---|---|---|---|---|
| Theoretical | 28.6 | 2.5 | 54.3 | 3.35 |
| Found | 28.9 | 2.6 | 53.8 | 3.28 |

### EXAMPLE 6

A solution of 2.1 g. $(C_2H_5O)_4Si$, 6.7 g. of perfluoropinacol and 1.0 g. of dimethylaminoethanol in 10 g. of o-xylene was heated at boiling which caused the formation of a dense white crystalline solid. This crystalline material was washed twice with hot xylene, once with hexane, and then evacuated to constant weight. The product

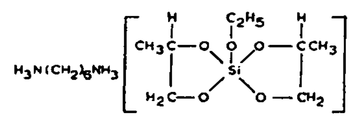


was found to have a neutral equivalent of 782 (theoretical 781). Elemental analysis of the product gave the following results:

| | %C | %H | %F |
|---|---|---|---|
| Theoretical | 24.6 | 1.41 | 58.4 |
| Found | 24.7 | 1.88 | 60.3 |

### EXAMPLE 7

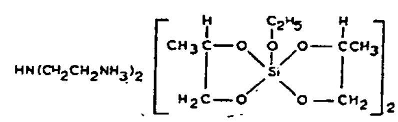
A solution of 20.8 g. of $(C_2H_5O)_4Si$, 19 g. of propylene glycol and 13.2 g. of hexamethylenediamine in 50 g. of acetonitrile was heated at reflux for 100 hours during which time by-produced ethanol was removed. Upon cooling overnight in a refrigerator, a white solid precipitated. This solid was filtered with the aid of a rubber dam, to protect it from the atmosphere, and evacuated to constant weight. The product



was found to have a neutral equivalent of 281 (theoretical 280). The product has no melting point, i.e., it decomposes before melting.

### EXAMPLE 8

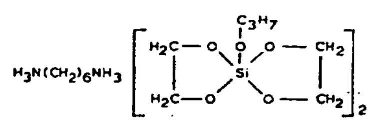
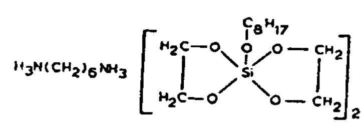
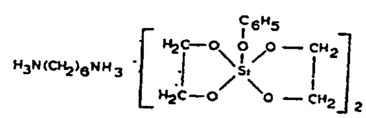
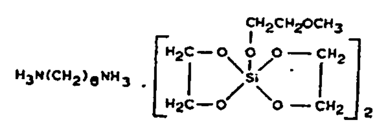
A solution of 83.2 g. of $(C_2H_5O)_4Si$, 76 g. of propylene glycol and 41.2 g. of diethylenetriamine in 70 cc. of acetonitrile was heated at reflux for one hour and then allowed to stand in a refrigerator for four days whereupon a crystalline material formed. This material was isolated and then washed, first with acetonitrile, then with tetrahydrofuran, then with hexane, finally with pentane, and then evacuated to constant weight. The product



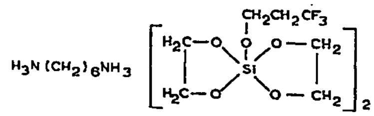
was found to have a neutral equivalent of 182 (theoretical 191). The product, like that of Example 7, has no melting point.

### EXAMPLE 9

When the silicates listed below are substituted for the ethylsilicate of Example 4, the indicated products are obtained.

| *Silicate* | *Product* |
|---|---|
| (A) $(C_3H_7O)_4Si$ |  |
| (B) $(C_8H_{17}O)_4Si$ |  |
| (C) $(C_6H_5O)_4Si$ |  |
| (D) $(CH_3OCH_2CH_2O)_4Si$ |  |

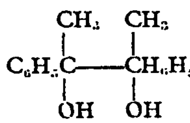
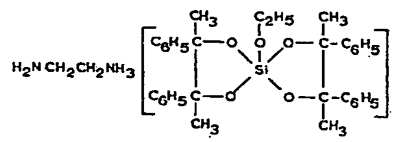
(E) $(CF_3CH_2CH_2O)_4Si$

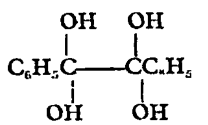
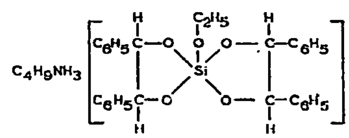


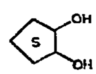
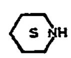
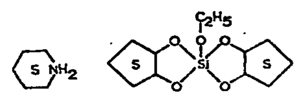
EXAMPLE 10

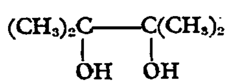
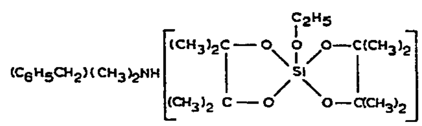
When $(C_2H_5O)_4Si$ is reacted with the vicinal aliphatic diols and amines listed below using the general procedure of Example 2, the following products are obtained:—

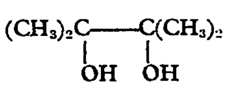
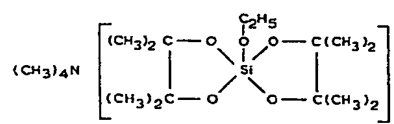
*Diol* — *Amine* — *Product*

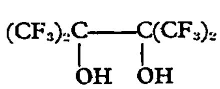
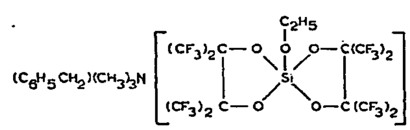
(A)  $H_2NCH_2CH_2NH_2$ 

(B)  $C_4H_9NH_2$ 

(C)   

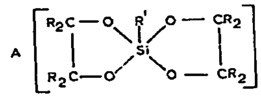
(D)  $(C_6H_5CH_2)(CH_3)_2N$ 

(E)  $(CH_3)_4NOH$ 

(F)  $(C_6H_5CH_2)(CH_3)_3NOH$ 

The complexes of this invention are useful as latent catalyst-hardeners for urethane polymers as will be illustrated by the following example.

This use is more fully described in our co-pending application No. 51430/67 (Serial No. 1,208,907) which relates to a curable polyurethane composition comprising (1) a curable polyurethane prepolymer and (2) a penta-coordinate silicon complex of the general formula



wherein each R is a hydrogen atom or a

monovalent radical attached to the carbon atom via a carbon-to-carbon bond R′ is a monovalent radical attached to the silicon atom via a carbon-to-silicon bond or a carbon-to-oxygen-to-silicon bond, and A is a cation formed from an amine containing an active hydrogen atom, there being a sufficient amount of (2) present to cause (1) to cure upon heating of the composition.

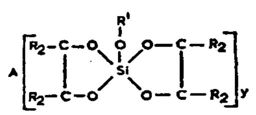
EXAMPLE 11

The complex of Example 4 was mixed with a commercial isocyanate terminated polyurethane prepolymer at a 4.3 to 10 weight ratio. The prepolymer had an NCO content of 10.6% by weight and an equivalent weight per NCO group of 396. The resulting heavy paste-like mixture was used to adhere two untreated aluminium panels using a one-half inch overlap. This combination was cured for 5 minutes at 350°F. (177°C.) and then the strength of the bond measured by pulling the panels at 180° to each other. This is a standard "lap-shear" test. This bond has 2128 pounds per square inch strength showing the complex had done an excellent job of curing the prepolymer.

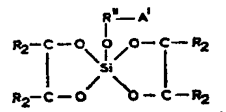
WHAT WE CLAIM IS:—

1. A pentacoordinate silicon complex of the general formula

(1)



or



(2)

in which each R is a hydrogen atom or a monovalent radical attached to the carbon atom via a carbon to carbon bond or two R radicals on adjacent carbon atoms may taken together represent a divalent radical attached to the adjacent carbon atoms via carbon to carbon bonds;

R′ is a monovalent radical attached to the oxygen atom via a carbon to oxygen bond;

A is a cation formed from an amine or ammonia;

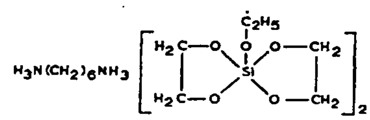
y is an integer equal to the valency of the cation A;

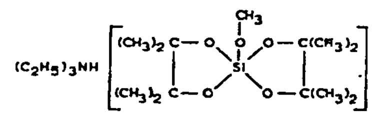
R″ is a divalent radical attached to the oxygen atom via a carbon to oxygen bond; and

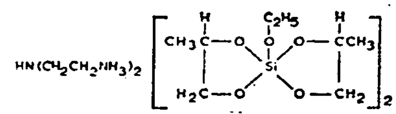
A′ is a quaternary ammonium group.

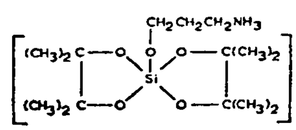
2. A complex as claimed in claim 1 wherein each R is a hydrogen atom or a monovalent hydrocarbon radical or two R radicals on adjacent carbon atoms taken together represent a divalent hydrocarbon radical and R′ is an alkyl radical with from 1 to 6 carbon atoms or R″ is an alkylene radical with from 1 to 6 carbon atoms.

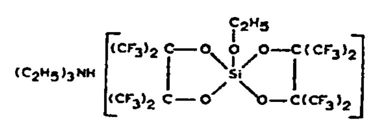
3. A complex as claimed in claim 1 which has the formula

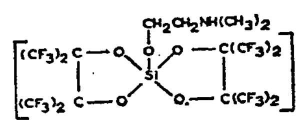












or

4. A pentacoordinate silicon complex substantially as hereinbefore described with reference to any of examples 1 to 10.

5. A method for preparing a pentacoordinate silicon complex of formula 1 as defined in claim 1 which comprises reacting

1) a compound of the formula $(R'O)_4$ Si wherein R′ is as defined in claim 1;

2) a vicinal aliphatic diol of the formula

$$\begin{array}{c} R_2\,C\,OH \\ | \\ R_2\,C\,OH \end{array}$$

wherein R is as defined in claim 1; and

3) ammonia or an amine.

6. A method for preparing a pentacoordinate silicon complex of formula 2 as defined in claim 1 which comprises reacting

1) a compound of the formula $(R'''O)_4$ Si where R''' is a monovalent radical attached to the oxygen atom via a carbon to oxygen bond;

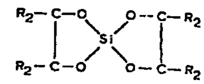
2) a vicinal aliphatic diol of the formula

$$\begin{array}{c} R_2COH \\ | \\ R_2COH \end{array}$$

wherein R is as defined in claim 1; and

3) an amino alcohol of the formula OH R''A'' wherein R'' is as defined in claim 1 and A'' is an amino group which on quaternisation gives the quaternary ammonium group A'.

7. A method for preparing a pentacoordinate silicon complex as defined in claim 1 which comprises reacting a silicon compound of the formula



wherein each R is as defined in claim 1 with either (1) an alcohol of the formula R'OH wherein R' is as defined in claim 1 and ammonia or an amine; or (2) an amino alcohol of formula OH—R''—A'' wherein R'' is as defined in claim 1 and A'' is an amino group which on quaternisation gives the quaternary ammonium group A'.

8. A pentacoordinate silicon complex when prepared by a process as claimed in any of claims 5 to 7.

9. A urethane polymer cured with a pentacoordinate silicon complex as claimed in any of claims 1 to 4 and 8.

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